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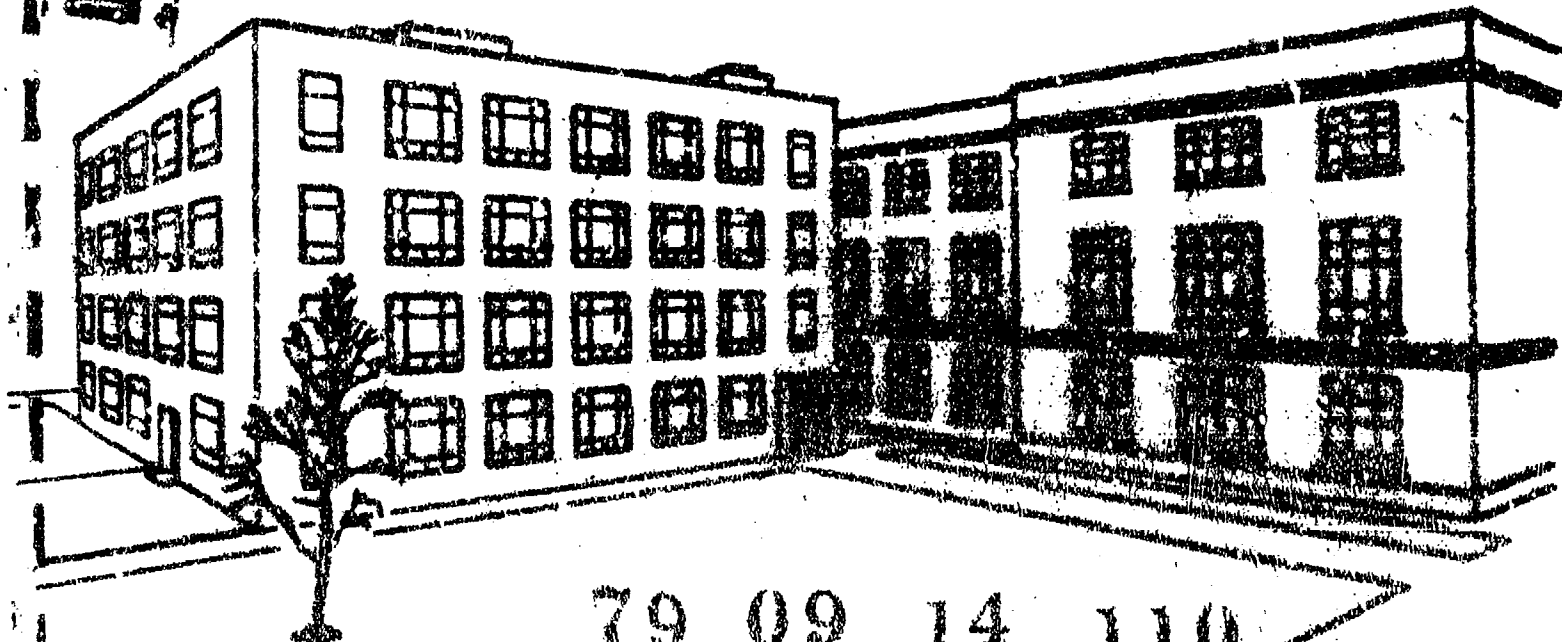
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BY R R BALDWIN AND R W WALKER

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ROBERT R. BALDWIN
RAYMOND W. WALKER

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
1. Refinement of the rate constants obtained from studies of the H_2+O_2 reaction at 500°C has continued. 2. Rate constants for the reactions of H atoms and OH radicals with C_2-C_5 alkanes have been refined, and Arrhenius parameters obtained. New studies have been made of the addition of 2,2,3,3-tetramethylbutane and 2,2,3-trimethylbutane to slowly reacting mixtures of H_2+O_2 at 480°C. 3. The mechanism of CO_2 formation in propionaldehyde oxidation, and of acetone formation in isobutyraldehyde oxidation at 440°C has been examined. Rate constants have been obtained for the initiation process and for attack of HO_2 at the various C-H

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bonds. 4. The homogeneous decomposition of 2,2,3,3-tetramethylbutane in the presence of O_2 has provided a source of HO_2 radicals and preliminary rate constants for HO_2+TMB, and for HO_2+C_2H_6 have been obtained at 440°C. The Thermochemistry of the t-butyl radical, and its reaction with H_2 and O_2 have been discussed. 5. Interpretation of the N_2O+H_2 reaction continues.

Plus

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Kinetics of Hydrogen-Oxygen and Hydrocarbon-Oxygen Reactions

1st April 1977 - 30th June 1979

by Baldwin, R. R., and Walker, R. W.

Chemistry Department,
The University,
HULL.

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INTRODUCTION

The reaction of a hydrocarbon with oxygen is a complex process involving the formation of a large number of products which themselves influence the oxidation, particularly as they are usually more reactive than the parent material. As a consequence, the whole process is highly autocatalytic under many conditions, and the nature and concentration of the radicals vary sharply as the reaction proceeds. There are also regions where cool flames and ignition occur. These conditions are not suitable for the elucidation of the elementary reaction steps and evaluation of rate constants, as is illustrated by the remarkably small amount of quantitative information that has been obtained by direct studies of hydrocarbon oxidation despite the large number of investigations that have been made.

Over a number of years, the Hull group has been concerned with devising systems and conditions which permit the evaluation of the elementary steps in hydrocarbon oxidation. Three main approaches have been made.

1.   The mechanism of the $H_2 + O_2$ reaction is well established in the temperature range around $500^{\circ}C$, and rate constants for the reactions involved have been determined accurately. The reaction thus forms a controlled environment in which to study the behaviour of an additive introduced in concentrations sufficiently small to avoid significant disturbance of the radical concentrations. Information can be obtained, first on the rate constants for the reaction of the radicals H and OH with the additive, and secondly on the reactions by which the radical formed from the parent material gives rise to the final products. The advantages of this approach are that the radical environment is under control, that a wide variety of additives can be made to undergo reactions at the same temperature, and that the intermediates believed to be important can be studied individually with the confidence that the radical environment is unaltered.

2.   The oxidation of aldehydes in the range $150-300^{\circ}C$ is a complex process, in which peracids play an important role. At temperatures above $400^{\circ}C$, however, a much simpler mechanism operates, since the main products, an alkene and carbon monoxide, are much less reactive than the parent aldehyde, so that the complications inherent in the direct oxidation of alkanes do not

occur. The reaction is slightly autocatalytic due to dissociation of the reaction product, hydrogen peroxide, a fortunate situation that permits evaluation of the initiation rate for aldehyde + oxygen, and also enables the rate constant for HO_2 + aldehyde to be determined. The carbonyl radical RCO readily decomposes at these temperatures to R + CO, so that reactions of alkyl radicals can be studied.

3. Because of the strain in the central C-C link, the compounds 2,2,3,3-tetramethylbutane (TMB), and 2,2,3-trimethylbutane (TRIMB), decompose by C-C homolysis at temperatures much lower than most alkanes, and the rate of production of radicals by this process is faster by a factor of 10^2 to 10^3 than by the reaction of the hydrocarbon with oxygen, even at atmospheric pressure of oxygen. The decomposition is thus a source of t-butyl radicals in the case of TMB, and of t-butyl and i-propyl radicals in the case of TRIMB, thus enabling the reactions of these radicals to be studied. In the presence of oxygen, both these radicals react predominantly (99%) to give the HO_2 radical so that a convenient source of this radical over the temperature range 420-560°C is available.

These three approaches are complementary and all can be used to advantage in elucidating the complex processes involved in hydrocarbon oxidation. In many cases, simultaneous use of these methods has prevented wrong conclusions being drawn.

By use of these methods it has been shown that four main types of reaction account for the majority of products in hydrocarbon oxidation at 450-550°C.

(a) Reaction of the alkyl radical with oxygen to form the conjugate alkene.

(b) Decomposition of the alkyl radical to a lower alkene and a smaller alkyl radical.

(c) Isomerisation of the alkylperoxy radical by internal hydrogen abstraction to form a hydroperoxyalkyl radical, which subsequently decomposes to give oxygenated ring compounds.

(d) Reaction of the hydroperoxyalkyl radical with oxygen to give lower aldehydes and ketones.

A body of rate constants for these four types of reaction is being built up and the patterns involved are beginning to emerge. It should thus be

possible to use these patterns to provide rate constants for computer modelling of the initial stages of hydrocarbon oxidation for hydrocarbons which have not been studied experimentally. The possibility has already been examined in the case of n-pentane.

As already pointed out, alkenes are an early product of alkane oxidation, and a full computer modelling of hydrocarbon oxidation requires an understanding of the mechanism of alkene oxidation. This process is even more complex than alkane oxidation, since both radical addition and radical abstraction reactions are possible, and the full range of approaches already described will certainly be needed. Some preliminary studies of the problem of alkene oxidation have already been made.

Details of individual studies are given in the following pages.

1. The hydrogen + oxygen reaction

Previously published rate constants for the very important elementary steps in the reaction between H_2 and O_2 have been evaluated with increased accuracy by allowing for the effect of self-heating in the system, the reaction of O atoms with hydrogen peroxide, and other minor refinements in the mechanism. The results indicate that, in most cases, the changes in the parameters due to the above effects are less than 10%, and the new values are summarised in Table 1 below.

Table 1
Rate Constant Ratios in $H_2 + O_2$ Reaction at 500°

$k_8/k_2 k_{10}^{\frac{1}{2}}$	= 0.53	$(dm^3 mol^{-1} s^{-1})^{-\frac{1}{2}}$
$k_{8a}/k_2 k_{10}^{\frac{1}{2}}$	= 0.081	$(dm^3 mol^{-1} s^{-1})^{-\frac{1}{2}}$
$k_{11}/k_{10}^{\frac{1}{2}}$	= 0.0366	$(dm^3 mol^{-1} s^{-1})^{\frac{1}{2}}$
k_{14}/k_2	= 281	
k_{14a}/k_2	= 34	
k_{15}/k_1	= 4.5	

$$OH + H_2 = H_2O + H \quad (1)$$
$$H + O_2 = OH + O \quad (2)$$
$$H + HO_2 = 2OH \quad (8)$$
$$H + HO_2 = H_2 + O_2 \quad (8a)$$
$$HO_2 + HO_2 = H_2O_2 + O_2 \quad (10)$$
$$HO_2 + H_2 = H_2O_2 + H \quad (11)$$
$$H + H_2O_2 = H_2O + OH \quad (14)$$
$$H + H_2O_2 = H_2 + HO_2 \quad (14a)$$
$$OH + H_2O_2 = H_2O + HO_2 \quad (15)$$

By use of the accurately known values of k_1, k_2 and k_{10}, and by combining the present results with data at other temperatures, the Arrhenius expressions in Table 2 are recommended. Information in the literature on reactions (14) and (14a) at lower temperatures is conflicting, and the alternative interpretations are discussed in a recently published paper.[1]

<center>**Table 2**</center>

<center>Recommended Arrhenius Parameters for Reactions in $H_2 + O_2$ System</center>

				$E/kJ\ mol^{-1}$	$A/(dm^3 mol^{-1} s^{-1})$
H + HO_2	=	2OH		7.6	5.4×10^{11}
H + HO_2	=	H_2 + O_2		0	2.8×10^{10}
H + HO_2	=	H_2O + O		7.6	5.5×10^{10}
HO_2 + H_2	=	H_2O_2 + H		90.0	2.0×10^9
OH + H_2O_2	=	H_2O + HO_2		4.8	3.7×10^9

Studies of the addition of CO to slowly reacting mixtures of
$H_2 + O_2$ have enabled values to be obtained for the rate constants for
reactions of OH and HO_2 radicals with CO at $500^{\circ}C$. These reactions
are of particular interest in the problem of atmospheric chemistry and
automobile engine pollution, and conflicting values of k_{22} in particular
have been published. Two types of study have been made, first the yields
of CO_2 when small amounts ($\frac{1}{2}$1%) of CO are added, and secondly, the effect
of large amounts of CO on the induction period and maximum rate of the
slow reaction. Values of $k_{21}/k_1 = 0.235 \pm 0.02$, $k_{22}/k_{10}^{\frac{1}{2}} = 0.42 \pm 0.03$
$(dm^3\ mol^{-1}s^{-1})^{\frac{1}{2}}$ have been obtained at $500^{\circ}C$, which combined with the
accurately known values of k_1, k_{10}, give $k_{21} = 0.96 \times 10^8\ dm^3\ mol^{-1}s^{-1}$,
$k_{24} = 1.9 \times 10^4$. Arrhenius parameters $A_{24} = 5.8 \times 10^{10}\ dm^3\ mol^{-1}s^{-1}$,
$E_{24} = 96.0\ kJ\ mol^{-1}$ are recommended. This work has been published.[2]

OH	+	CO	$\approx$	CO_2	+	H	(21)
HO_2	+	CO	=	CO_2	+	OH	(22)

2. **Addition of hydrocarbon to slowly reacting mixtures of hydrogen**
and oxygen

(a) **Rate constants for reaction of H atoms and OH radicals with alkanes**

Results previously reported[3] for the rate constants for reaction of
H atoms and OH radicals with the hydrocarbons ethane, propane, n- and
i-butane, and n- and neo-pentane have been re-examined to allow for the
pressure changes due to the oxidation of the hydrocarbon, self-heating
of the reaction mixture, and removal of the hydrocarbon by attack of O
atoms and of HO_2 radicals. A computer treatment has enabled all these
complications to be analysed. Although no single factor has a major
effect, the combined effect is to reduce the rate constant for OH attack

by a factor of approximately 2, whereas the value for H attack is almost unaltered.

$$OH + H_2 = H_2O + H \quad (1)$$
$$H + O_2 = OH + O \quad (2)$$
$$OH + RH = H_2O + \stackrel{..}{R} \quad (3)$$
$$H + RH = H_2 + R \quad (4)$$

Examination of the results indicates that the total rate constant for radical attack on an alkane can be obtained by summing the contributions from attack at the three different types of C-H bond, primary, secondary and tertiary, in the molecule. Combination with data by Greiner[4] at lower temperatures for OH attack enables the Arrhenius parameters A_3/A_1 and $(E_1 - E_3)$ to be obtained for each type of bond. The data for C_2-C_5 alkanes are self-consistent, and examination indicates that the overall rate constant ratio k_3/k_1 can be expressed by equation (i).

$$k_3/k_1 = 0.214n_p \exp(1070/T) + 0.173n_s \exp(1820/T) + 0.273n_t \exp(2060/T) \quad (i)$$

where n_p, n_s and n_t are the number of primary, secondary and tertiary C-H bonds in the molecule. Similar treatment of the data for H atoms gives the expression (ii) for the ratio k_4/k_2 at 480°C.

$$k_4/k_2 = 7.0n_p + 43n_s + 160n_t \quad (ii)$$

Absolute values of k_3 and k_4 can be obtained by substituting the known values of k_1 and k_2 in expressions (i) and (ii). Data on rate constants at other temperatures are more limited for H than for OH, but on the basis of the data available, the following Arrhenius parameters are recommended.

Table 3

Arrhenius Parameters for H Abstraction by H Atoms from Alkane

Type of bond	$E_4/kJ\ mol^{-1}$	A_4 per C-H bond $dm^3 mol^{-1}s^{-1}$
primary	39.2	2.2×10^{10}
secondary	33.3	4.9×10^{10}
tertiary	25.2	5.1×10^{10}

To deduce the mechanism of product formation in alkane oxidation, it is necessary to know the proportions of the various radicals formed by H and OH attack on the alkane, and equations (i) and (ii) provide the best available method. However, this procedure may be less reliable if

there is a high degree of branching in the molecule. This is shown by some experimental studies re-ently made[5] with 2,2,3,3-tetramethylbutane as additive. The rate constant ratios k_3/k_1 and k_4/k_2 at 480°C are given below for this hydrocarbon and for neopentane and ethane, which also contain only primary C-H bonds.

Table 4
Rate Constant Ratios for H + RH and OH + RH at 480°C

Hydrocarbon	k_3/k_1	k_4/k_2
ethane	5.7 ± 0.5	44 ± 4
neopentane	10.0 ± 1.0	52 ± 5
tetramethylbutane	8.0 ± 1.0	112 ± 8

On a simple additivity basis, these results should each be in the ratio 1:2:3.

(b) Reactions of alkyl radicals

The second object of studies of the addition of small amounts of a hydrocarbon to slowly reacting mixtures of $H_2 + O_2$ is to obtain information on the reactions of the radicals produced from the alkane, and the mechanism of formation of the various products. The advantages of this approach over direct studies of alkane oxidation have been discussed elsewhere, and include the fact that the radical concentration is controlled by the $H_2 + O_2$ system rather than the alkane, the fact that a wide range of concentrations can be investigated under essentially identical conditions, and that primary and secondary products can easily be distinguished.

Studies with a range of alkanes have clarified considerably the mechanism of oxidation and suggested that the main products in alkane oxidation at temperatures around 500°C result from four major types of reaction.
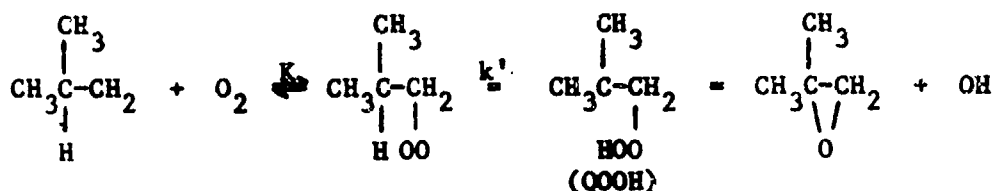
(i) Decomposition of the alkyl radical to a lower alkene and a smaller alkyl radical.

(ii) Formation of conjugate alkenes by the reaction of the alkyl radical with O_2, for example:

$$n\text{-}C_3H_7 + O_2 = C_3H_6 + HO_2 \qquad (5p)$$

Although this reaction may occur through addition of O_2 to the alkyl radical to form the RO_2 radical, followed by decomposition to give the alkene + HO_2, this path is kinetically identical to reaction (5p), since

R and RO_2 are almost always equilibrated, and the bimolecular form (5p) is preferred.

(ii) Addition of O_2 to form the RO_2 radical followed by isomerisation to give a peroxyalkyl radical (QOOH) and decomposition to give an oxygen-ring compound. This is illustrated by the formation of isobutene oxide from isobutyl radicals.

$$
CH_3\underset{H}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}\text{-}CH_2 \;+\; O_2 \;\overset{K}{\rightleftharpoons}\; CH_3\underset{H}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}\text{-}\underset{OO}{\overset{}{CH_2}} \;\overset{k'}{=}\; CH_3\underset{HOO}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}\text{-}CH_2 \;=\; CH_3\overset{CH_3}{\underset{\underset{O}{\diagdown\diagup}}{\overset{|}{C}}}\text{-}CH_2 \;+\; OH
$$

(QOOH)

As shown in previous papers, the overall rate constant for this reaction is given by expression (iii)

$$k = Kk' \tag{iii}$$

where K is the equilibrium constant for the $R + O_2 = RO_2$ equilibrium.

(iv) Reaction of the peroxyalkyl radical (QOOH) with O_2 to give oxygenated products, such as aldehydes and ketones.

With the completion of studies, now published,[6] with i-butane as additive, rate constants for a number of specific radicals giving specific alkenes have been obtained, and these are summarised in Table 5. The studies with i-butane have been particularly important in two respects. First, a value of $k_5 = 6.8 \times 10^7$ has been obtained which, when combined with a low temperature measurement gives $A_5 = 6.9 \times 10^9$ dm^3 $mol^{-1}s^{-1}$, $E_5 = 29$ kJ mol^{-1}. No other determinations of the Arrhenius parameters for conjugate alkene formation exist. From measurements of the relative yields of isobutene oxide and 3-methyloxetan, a value of $k_6/k_7 = 4.1 \pm 0.4$ is obtained. Use of the rather uncertain value of the rate constant for the decomposition of i-butyl radicals, together with the best thermochemical data available for reaction (8), gives $k_6 = 1.83 \times 10^5$ s^{-1}, $k_7 = 4.45 \times 10^4$ s^{-1} at 480°C. No other experimental value is available for k_6 nor for any similar reaction involving the transfer of a tertiary H atom. Rate constants for the isomerisation of RO_2 radicals to QOOH radicals are summarised in Table 6.
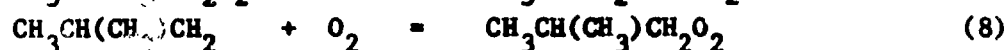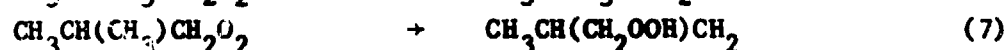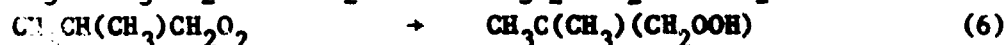
$$CH_3CH(CH_3)CH_2 \;+\; O_2 \;=\; (CH_3)_2C\text{=}CH_2 \;+\; HO_2 \tag{5}$$

$$CH_3CH(CH_3)CH_2O_2 \;\rightarrow\; CH_3C(CH_3)(CH_2OOH) \tag{6}$$

$$CH_3CH(CH_3)CH_2O_2 \;\rightarrow\; CH_3CH(CH_2OOH)CH_2 \tag{7}$$

$$CH_3CH(CH_3)CH_2 \;+\; O_2 \;=\; CH_3CH(CH_3)CH_2O_2 \tag{8}$$

Table 5

Rate Constants for the formation of Conjugate Alkene

Reaction	Product	$T/^{\circ}C$	$k/dm^3\ mol^{-1}\ s^{-1}$
$C_2H_5 + O_2$	C_2H_4	440	$6... \times 10^7$
		623	1.0×10^8
$n\text{-}C_3H_7 + O_2$	C_3H_6	480	7.1×10^7
$i\text{-}C_3H_7 + O_2$	C_3H_6	440	1.27×10^8
$n\text{-}C_4H_9 + O_2$	$C_4H_8\text{-}1$	480	1.6×10^8
$s\text{-}C_4H_9 + O_2$	$trans\text{-}C_4H_8\text{-}2$	480	7.8×10^7
	$cis\text{-}C_4H_8\text{-}2$	480	4.3×10^7
	$C_4H_8\text{-}1$	480	5.1×10^7
$i\text{-}C_4H_9 + O_2$	$i\text{-}C_4H_8$	480	6.8×10^7
$t\text{-}C_4H_9 + O_2$	$i\text{-}C_4H_8$	480	1.8×10^8

Table 6

Rate Constants for the formation of QOOH Radicals

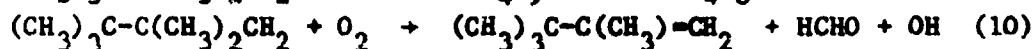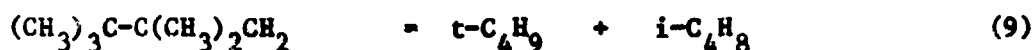| C-H bond broken	Type of H atom transfer[a]	k/s^{-1} at 480°C	$E^b/kJ\ mol^{-1}$
	1,3p	$(1.3 \times 10^1)^c$	159
	1,4p	2.2×10^3	125
primary	1,5p	1.8×10^4	113
	1,6p	6.0×10^4	105
	1,7p	9.3×10^4	103
	1,3s	(1.4×10^2)	144
secondary	1,4s	2.4×10^4	111
	1,5s	3.0×10^5	95
	1,6s	(6.5×10^5)	90
	1,3t	1.5×10^3	130
tertiary	1,4t	1.9×10^5	98
	1,5t	(2.2×10^5)	84
	1,6t	(7.1×10^6)	75

[a] In this table, p, s, t refer to abstraction from primary, secondary and tertiary C-H bonds, and the adjacent numbers refer to the position of the atom abstraction as illustrated below for a 1,5p transition.
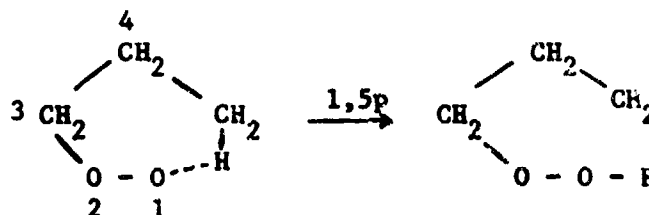

[b] Calculated using $A = 10^{12.1}\ s^{-1}$, the value suggested by Benson for a 1,5 transfer. It has been suggested, however, that the value of A decreases as the ring size increases.

[c] Values in brackets are estimates, based on the experimental values.

A complete analysis of the products when the highly branched alkane 2,2,3,3-tetramethylbutane (TMB) is the additive has been made at $480^{\circ}C$ over a wide range of mixture composition. Isobutene in about 95% yield is the only major initial product, although small amounts (ca. 1%) of propene, 2,3,3-trimethylbutene-1, isobutene oxide, formaldehyde and methane are also formed. No evidence has been found for the presence of O-ring compounds containing the same number of carbon atoms as TMB. Thus, even at pressures of O_2 approaching atmospheric, the TMB radical $((CH_3)_3C-C(CH_3)_2CH_2)$ breaks down almost completely by the dissociation reaction (9) at $480^{\circ}C$. By measuring the yields of (propene + 2,3,3-trimethylbutene-1) relative to i-butene as a function of O_2 concentration, the ratio k_9/k_{10} has been obtained. From a reasonable estimate of k_{10}, based on analogous reactions,[*] $k_9 \approx 1.9 \times 10^6 \ s^{-1}$ at $480^{\circ}C$. This value is a factor of 10-100 times greater than the values of rate constants for the C-C homolysis of $n-C_3H_7$, $s-C_4H_9$, $i-C_4H_9$ and $neo-C_5H_{11}$ radicals, presumably because of the considerable strain in the central C-C bond in the TMB radical.

$$(CH_3)_3C-C(CH_3)_2CH_2 \quad = \quad t-C_4H_9 \quad + \quad i-C_4H_8 \qquad (9)$$
$$(CH_3)_3C-C(CH_3)_2CH_2 + O_2 \quad \rightarrow \quad (CH_3)_3C-C(CH_3)=CH_2 \quad + HCHO + OH \quad (10)$$

From the yields of 2,3,3-trimethylbutene-1, the rate constant k_{11} has been obtained as $1.1 \times 10^4 \ s^{-1}$, close to the expected value for loss of a methyl radical by C-C homolysis. No rate constants for the decomposition processes k_9 and k_{11} were previously available.

$$(CH_3)_3C-C(CH_3)_2CH_2 \quad = \quad (CH_3)_3C-C(CH_3)=CH_2 \quad + \quad CH_3 \qquad (11)$$
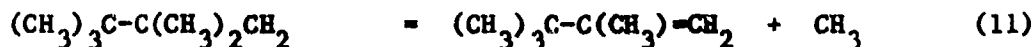
In the case of propylperoxy, neopentylperoxy and all four species of butylperoxy radical, the hydroperoxyalkyl radicals (QOOH) formed by internal H-atom transfer, either decompose by loss of OH and then cyclise to give an O-ring compound, or add a further molecule of O_2 before decomposing. No evidence has been found for either of these types of reaction in the case of the QOOH radical formed from tetramethylbutylperoxy radicals, and it appears to react uniquely by β- and γ-scission to give lower alkenes, as illustrated by the reaction below.

---

[*] Reaction (10), though represented kinetically by the equation .en, proceeds through formation of the peroxyradical, isomerisation to a peroxyalkyl radical, and subsequent decomposition, as already discussed.

$$(CH_3)_3C-C(CH_3)_2(CH_2OOH) \rightarrow i-C_4H_8 + C_3H_6 + HCHO + OH$$
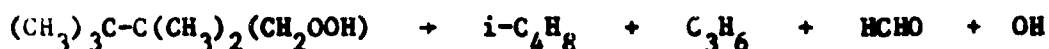
The shift to C-C scission reactions in the case of QOOH radicals formed from TMB must thus be associated with the steric strain in the central C-C bond.

This work has now been published.[5]

A detailed study has been made using 2,2,3-trimethylbutane as additive. The rate of removal by radical attack is somewhat greater than for TMB because of the presence of a tertiary C-H group, and computer treatment is being used to evaluate the total rate constants for H and OH attack. The mechanism of product formation is more complex than that for TMB because three different species of alkyl radical are formed by radical attack on the additive. Using the additivity principle expressed by equations (i) and (ii) the proportions of the three radicals can be calculated. The major initial products are $i-C_4H_8$ and C_3H_6 formed in almost equal yields of about 85%. Detailed interpretation is proceeding with a view to an evaluation of the rate constants of the reactions involved.

With n-pentane as additive, a full analysis of the reaction products over a wide range of mixture composition has been completed. For this system, no specific rate constants, except for H and OH with C_5H_{12}, are available for any of the elementary reactions involved. However, by use (without modification) of rate constants obtained from studies with C_2-C_4 alkanes and neopentane, it is possible to predict the initial yields of all major products from pentane to better than a factor of 2 over a wide range of mixture composition.[7] The agreement may be improved, of course, by minor modifications in the values of the rate constants. However, the possibility of the general use of rate constants determined for specific reactions is of great importance to computer modelling of complex systems, where it is extremely unlikely that a major proportion of the rate constants is known accurately.
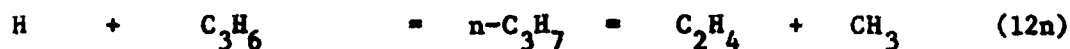
(c) Addition of alkenes

Previous studies of the addition of alkenes to slowly reacting mixtures of $H_2 + O_2$ have shown that conjugate and lower alkenes are the major primary products, sometimes in yields of over 80%, in the oxidation of C_2-C_5 alkanes over the temperature range 400-500°C. A full computer

modelling of the oxidation process for alkanes thus requires an understanding of the mechanism of alkene oxidation. This oxidation is more complex than the initial stages of alkane oxidation since radical addition to the alkene may occur as well as hydrogen abstraction by the radical. It is not surprising, therefore, that very few rate consants are available for the elementary processes involved. A number of different approaches will be required if the elementary reaction steps are to be disentangled. One such approach involves the addition of smallamounts of alkenes to slowly reacting mixtures of $H_2 + O_2$. As with alkane addition, two types of measurement can be made. Study of the loss of hydrocarbon at very low concentrations of additive provides information on radical attack of the alkene, whereas examination of the reaction products (for which a higher concentration of alkene is necessary to provide reasonable yields of products) gives information on the reactions of the radical produced by the primary attack.

With propene, the main primary products are methane, ethylene, formaldehyde, acetaldehyde, propene oxide, carbon monoxide and acrolein. The products methane, ethylene, formaldehyde and propene oxide can all be formed in reactions involving the initial addition of a radical to propene.

Ethylene and methane are almost certainly formed by decomposition of the $n-C_3H_7$ radical. Previous studies have shown that the oxidation of methyl radicals in a $H_2 + O_2$ environment at $480^{\circ}C$ can be represented kinetically by the reactions (14) and (15) which compete with reaction (13). The variation of the ratio [methane]/[ethylene] with mixture composition is virtually identical with that observed in other systems where methyl radicals are produced, and this suggests that reaction (12n) is the only significant source of both these products.

$$H \quad + \quad C_3H_6 \quad = \quad n-C_3H_7 \quad = \quad C_2H_4 \quad + \quad CH_3 \quad (12n)$$
$$CH_3 \quad + \quad H_2 \quad = \quad CH_4 \quad + \quad H \quad (13)$$
$$CH_3 \quad + \quad O_2 \quad + \quad M \quad = \quad \text{oxidation products (e.g. HCHO)} \quad (14)$$
$$CH_3 \quad + \quad O_2 \quad = \quad \text{oxidation products (e.g. HCHO)} \quad (15)$$
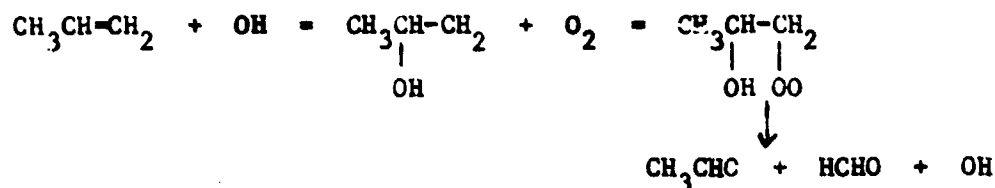
H-atom addition at the terminal position of the double bond will give the more stable $s-C_3H_7$ radicals. Studies of the oxidation of i-butyraldehyde, discussed later, show that $s-C_3H_7$ radicals react predominantly ($\ddagger99\%$) with O_2 to reform propene.

$$H \quad + \quad C_3H_6 \quad = \quad s\text{-}C_3H_7 \quad\quad\quad (12t)$$

$$s\text{-}C_3H_7 \quad + \quad O_2 \quad = \quad C_3H_6 \quad + \quad HO_2 \quad\quad (16)$$

Propene oxide is almost certainly formed through HO_2 addition to propene,

$$HO_2 \quad + \quad C_3H_6 \quad = \quad C_3H_6O \quad + \quad OH \quad\quad\quad (17)$$

The most likely mechanism for formation of acetaldehyde is by addition of an OH radical to propene, followed by reaction with O_2.

$$CH_3CH{=}CH_2 \; + \; OH \; = \; \underset{\underset{OH}{|}}{CH_3CH{-}CH_2} \; + \; O_2 \; = \; \underset{\underset{OH\;OO}{|\;\;|}}{CH_3CH{-}CH_2}$$

$$\downarrow$$

$$CH_3CHC \; + \; HCHO \; + \; OH$$

All the products so far discussed have been produced by radical addition reactions, and it seems likely that the remaining products, CO and acrolein, together with some of the formaldehyde are produced from the allyl radical obtained by H-abstraction from propene, though no simple reactions can be written for these products. Moreover, there is no evidence for the occurrence of reaction (18) which would produce allene as a product; this is consistent with the significant endothermicity of this reaction.
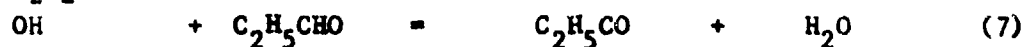
$$CH_2CH{=}CH_2 \quad + \quad O_2 \quad = \quad CH_2{=}C{=}CH_2 \quad + \quad HO_2 \quad\quad (18)$$
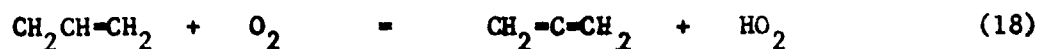
Other workers have suggested that the C-H bonds in the CH_3 group of propene are no stronger than the aldehydic C-H bond in aldehydes. However, if rate constants for H, OH and HO_2 abstraction from the aldehydic C-H bond are used, high rate constants for the addition reactions have to be used to obtain the high yields of addition products, and the rate of consumption of propene then becomes too high by a factor of about four. Further study of this problem is in progress.

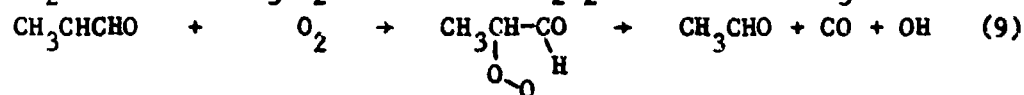3. The oxidation of aldehydes

(a) The oxidation of propionaldehyde

The oxidation of propionaldehyde at $440^{\circ}C$ in aged boric-acid-coated vessels[8] has been re-examined with a view to establishing the mechanism of formation of two important products, carbon dioxide and acetaldehyde, which are formed[8] in 5-15% yield, depending on mixture composition.

The main products, ethylene, carbon monoxide and hydrogen peroxide are accounted for by the basic mechanism given below.

$$C_2H_5CHO + O_2 = C_2H_5CO + HO_2 \quad (1)$$
$$C_2H_5CO + M = C_2H_5 + CO + M \quad (2)$$
$$C_2H_5 + O_2 = C_2H_4 + HO_2 \quad (3)$$
$$HO_2 + C_2H_5CHO = C_2H_5CO + H_2O_2 \quad (4)$$
$$HO_2 + HO_2 = H_2O_2 + O_2 \quad (5)$$
$$H_2O_2 + M = 2OH + M \quad (6)$$
$$OH + C_2H_5CHO = C_2H_5CO + H_2O \quad (7)$$

The autocatalysis observed in the reaction is attributed[8] to the decomposition of hydrogen peroxide by reaction (6), followed by reaction (7) of the OH radical.

Only a trace of acetaldehyde is formed from C_2H_5 radicals produced by addition of ethane to slowly reacting $H_2 + O_2$ mixtures, so that the reaction $C_2H_5 + O_2 = CH_3CHO + OH$, often used in mechanisms of hydrocarbon oxidation, is not the cause of acetaldehyde formation. It is almost certain that acetaldehyde is formed by radical attack at the secondary CH_2 position, followed by reaction of the radical with O_2.

$$HO_2 + CH_3CH_2CHO = H_2O_2 + CH_3CHCHO \quad (8)$$
$$CH_3CHCHO + O_2 \rightarrow CH_3\underset{\underset{O_{\diagdown}O}{|}}{CH}{-}\underset{H}{C}O \rightarrow CH_3CHO + CO + OH \quad (9)$$

This sequence is similar to the peroxyradical isomerisation and decomposition (PRID) mechanism given in section (2b).

The ratio $[CO_2]/[CO]$ in the products increases with increase in O_2 concentration, and decreases with increasing addition of inert gas, consistent with a competition between reactions (10) and (11), which gives expression (i) below.

$$d[CO_2]/d[CO] = k_{10}[O_2]/k_{11}[M] \quad (i)$$

$$C_2H_5CO + O_2 = C_2H_5CO_3 = C_2H_4 + CO_2 + OH \quad (10)$$
$$C_2H_5CO + M = C_2H_5 + CO + M \quad (11)$$
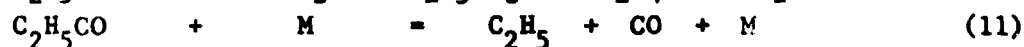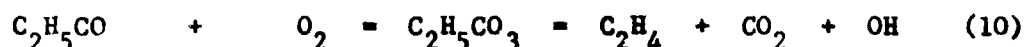
Detailed studies of the variation of $[CO_2]/[CO]$ ratio were made over a wide range of mixture composition, since the system appeared to offer a method of studying the interesting problem of the relative efficiency of

different molecules in reaction (11). However, the ratio $[CO_2]/[CO]$ was found to decrease sharply in the early stages of reaction, to an approximately constant value, and then to rise slowly after about 50% consumption of propionaldehyde. This decrease in the ratio was attributed to the simultaneous occurrence of a surface process forming carbon dioxide, which becomes less important as the chain reaction accelerates. The rise in the later stages of reaction is attributed to the oxidation of carbon monoxide by the radical OH and HO_2, and computer treatment confirms the importance of these reactions in the later stages. Confirmation of the existence of a surface formation of carbon dioxide is provided by the increased $[CO_2]/[CO]$ ratio in smaller diameter vessels, whereas the rate of formation of carbon monoxide is unaffected.

A detailed interpretation of the results for a wide range of mixture composition gives the rate constants at $440^{\circ}C$ listed in Table 7.

Table 7
Rate Constants at $440^{\circ}C$ in Propionaldehyde Oxidation

$$k_1 = 0.077 \text{ dm}^3 \text{ mol}^{-1}\text{s}^{-1}$$
$$k_4 = 1.59 \times 10^6 \text{ dm}^3 \text{ mol}^{-1}\text{s}^{-1}$$
$$k_8 = 1.1 \times 10^5 \text{ dm}^3 \text{ mol}^{-1}\text{s}^{-1}$$
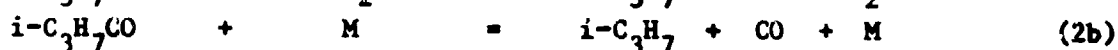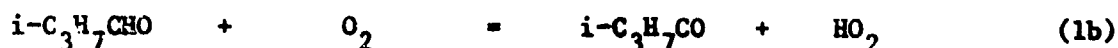$$k_{10}/k_2 = 0.108 \quad (M = N_2)$$

The value of k_4 is significantly higher, by a factor of about 4, than preliminary estimates for the rate constant of HO_2 with the secondary CH_2 group in propane, and this suggests that the secondary CH bond is weaker in propionaldehyde than in propane by about 8 kJ mol^{-1} because of the adjacent aldehydic group.
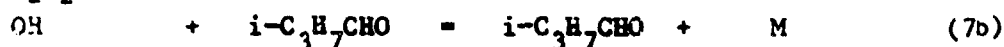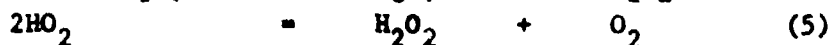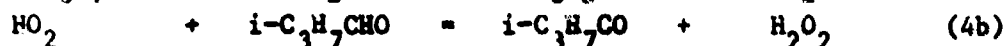
This work has been published.[9]

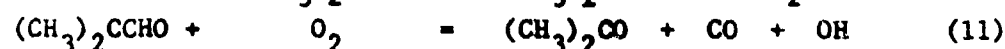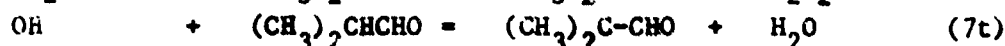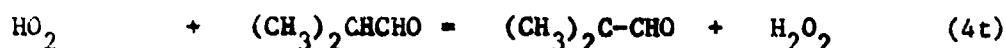(b) The oxidation of isobutyraldehyde at $440^{\circ}C$

The major products are propene, carbon monoxide and hydrogen peroxide, although small amounts of carbon dioxide (4%), propene oxide (1%), and acetone (in yields of 6-12% depending on mixture composition) are also found. The following scheme accounts for the main reaction products.

$$i\text{-}C_3H_7CHO + O_2 = i\text{-}C_3H_7CO + HO_2 \qquad (1b)$$
$$i\text{-}C_3H_7CO + M = i\text{-}C_3H_7 + CO + M \qquad (2b)$$

$$i\text{-}C_3H_7 \quad + \quad O_2 \quad = \quad C_3H_6 \quad + \quad HO_2 \quad (3b)$$

$$HO_2 \quad + \quad i\text{-}C_3H_7CHO \quad = \quad i\text{-}C_3H_7CO \quad + \quad H_2O_2 \quad (4b)$$

$$2HO_2 \quad = \quad H_2O_2 \quad + \quad O_2 \quad (5)$$

$$H_2O_2 \quad + \quad M \quad = \quad 2OH \quad + \quad M \quad (6)$$

$$OH \quad + \quad i\text{-}C_3H_7CHO \quad = \quad i\text{-}C_3H_7CHO \quad + \quad M \quad (7b)$$

The formation of acetone is attributed to reactions (4t), (7t) and (11) below. The increase in the percentage yield of acetone as the reaction proceeds may be used to obtain both k_{4t} and k_{7t}, since the rise in acetone yield is due to the increase in the concentration of the less selective OH radical, as a result of an increasing contribution from the dissociation of the product hydrogen peroxide (reaction 6). The increase in acetone concentration with increasing O_2 concentration is attributed to competition between reactions (11) and (12).

$$HO_2 \quad + \quad (CH_3)_2CHCHO \quad = \quad (CH_3)_2C\text{-}CHO \quad + \quad H_2O_2 \quad (4t)$$

$$OH \quad + \quad (CH_3)_2CHCHO \quad = \quad (CH_3)_2C\text{-}CHO \quad + \quad H_2O \quad (7t)$$

$$(CH_3)_2CCHO \quad + \quad O_2 \quad = \quad (CH_3)_2CO \quad + \quad CO \quad + \quad OH \quad (11)$$

$$(CH_3)_2CCHO \quad + \quad M \quad = \quad C_3H_6 \quad + \quad CHO \quad + \quad M \quad (12)$$

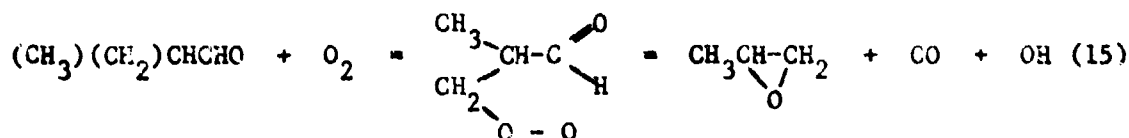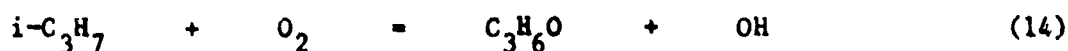$$HCO \quad + \quad O_2 \quad = \quad CO \quad + \quad HO_2 \quad (13)$$

Although the formation of acetone can be represented kinetically by reaction (11), it is undoubtedly formed by a peroxyradical isomerisation and decomposition (PRID) mechanism analogous to that responsible for the formation of acetaldehyde from propionaldehyde.

$$(CH_3)_2C\text{-}CHO + O_2 = (CH_3)_2C\text{-}C\text{-}C\overset{\diagup\!\!\diagup O}{\underset{H}{\diagdown}} = (CH_3)_2CO + CO + OH$$
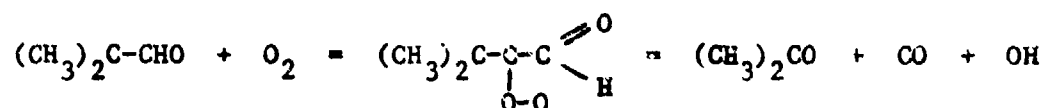
The full mechanism has been treated by a computer program using a Kutta-Runge integration process to examine the variation of the extent of reaction with time, which gives the rate constants $k_{1b} = 0.12 \pm 0.01 \ dm^3 \ mol^{-1} \ s^{-1}$, $k_{4b} = (1.8 \pm 0.1) \times 10^6 \ dm^3 mol^{-1} s^{-1}$ at 440°C. From the yields of acetone, the values $k_{4t} = (1.4 \pm 0.2) \times 10^5 \ dm^3 \ mol^{-1} \ s^{-1}$, $k_{7t}/k_{7b} = 0.7 \pm 0.1$, $k_{12}/k_{11} = 0.014 \pm 0.002$ (M = N_2) have been obtained. The value of k_{4t} is significantly higher than an upper limit of 4×10^4 found for HO_2 attack at the tertiary C-H bond in butane. This confirms the suggestion made in section (3a) that C-H bonds adjacent to an aldehydic group are noticeably weaker than the corresponding bond in an alkane.

Propene oxide is formed both from $i\text{-}C_3H_7$ radicals by reaction (14) and from the radicals formed by OH and HO_2 attack at the primary CH bonds.

$$i\text{-}C_3H_7 \quad + \quad O_2 \quad = \quad C_3H_6O \quad + \quad OH \quad \quad (14)$$

$$(CH_3)(CH_2)CHCHO + O_2 = \begin{array}{c} CH_3 \\ \diagdown \\ CH\text{-}C \diagup^{O} \\ \diagup \qquad \diagdown_H \\ CH_2 \\ \diagdown \\ O - O \end{array} = CH_3CH\text{-}CH_2 + CO + OH \ (15)$$

Allowance for the relatively small amount of propene oxide formed by reaction (15) is included in the computer treatment, which gives the best value of k_{14}/k_{3b} as 0.007. This is consistent with a value for 0.010 for the corresponding ratio for $t\text{-}C_4H_9$ radicals.

As found with propionaldehyde, the $[CO_2]/[CO]$ ratio falls sharply as the reaction proceeds, and then rises later due to secondary formation of carbon dioxide from carbon monoxide. This fall has been interpreted in terms of a heterogeneous formation of carbon dioxide in parallel with a homogeneous formation by isomerisation and decomposition of the $(CH_3)_2CHCO_3$ radical. However, the yield of carbon dioxide is much lower than in the case of propionaldehyde, and varies rather erratically, so that a detailed study of the mechanism of formation is not considered worthwhile.

This work has been accepted for publication.[10]

(c)   Summary of rate constants

Rate constants for the initiation reaction (1) and for the reaction (4) of HO_2 radicals with aldehydes are summarised below.

Table 8

Rate Constants in Aldehyde Oxidation

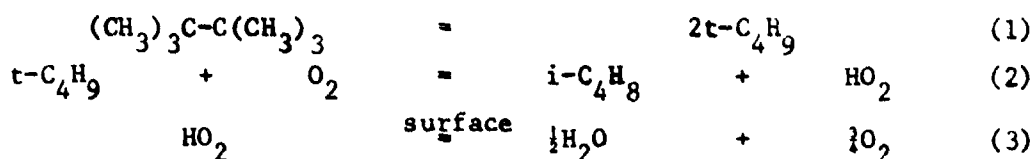| Aldehyde	k_1 $dm^3 mol^{-1} s^{-1}$	Position of HO_2 attack	k_4 $dm^3 mol^{-1} s^{-1}$	Temp. $^{\circ}C$
HCHO	0.022	aldehydic	$(5.6 \pm 0.5) \times 10^5$	440
C_2H_5CHO	0.081	aldehydic	$(1.52 \pm 0.15) \times 10^6$	440
		secondary CH_2	$(1.5 \pm 0.2) \times 10^5$	440
$n\text{-}C_3H_7CHO$		total	$(2.4 \pm 0.5) \times 10^6$	450
$i\text{-}C_3H_7CHO$	0.120	aldehydic	$(1.83 \pm 0.1) \times 10^6$	440
		tertiary C-H	$(1.4 \pm 0.2) \times 10^5$	440

As formaldehyde has two aldehydic C-H bonds, the much lower values both for k_1 and k_4 imply that the activation energy is 8-12 kJ mol^{-1} higher for reactions of HO_2 and of O_2 with formaldehyde compared with higher aldehydes, and a similar difference probably applies to the aldehyde C-H bond dissociation energies.

A paper[11] summarising these results and other rate constants for reactions of HO_2 radicals was presented at the Seventeenth International Combustion Symposium at Leeds in August 1978.

4. The oxidation of 2,2,3,3-tetramethylbutane

(a) The oxidation in KCl-coated vessels

Because of the considerable strain caused by the six CH_3 groups around the central C-C bond, the decomposition of 2,2,3,3-tetramethylbutane (TMB) occurs at temperatures $100-150^{\circ}C$ lower than needed for straight chain alkanes. The thermolysis of a hydrocarbon is normally a chain reaction, sensitive to surface effects, but these difficulties can be avoided in the case of TMB by carrying out the decomposition in the presence of O_2. Previous studies have shown that 99% of $t-C_4H_9$ radicals react with O_2 to form isobutene according to reaction (2). If the reaction is carried out in a KCl-coated vessel, known to be effective for the destruction of HO_2 radicals, the basic mechanism thus involves reactions (1)-(3).
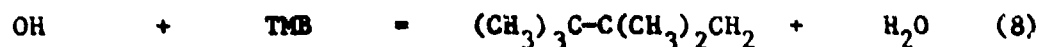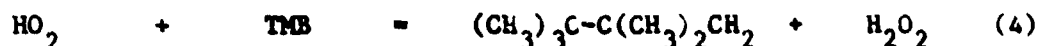
$$(CH_3)_3C-C(CH_3)_3 \quad = \quad 2t-C_4H_9 \quad (1)$$

$$t-C_4H_9 \quad + \quad O_2 \quad = \quad i-C_4H_8 \quad + \quad HO_2 \quad (2)$$

$$HO_2 \quad \xrightarrow{surface} \quad \tfrac{1}{2}H_2O \quad + \quad \tfrac{3}{4}O_2 \quad (3)$$

This mechanism gives the stoichiometric equation (s) and the relationships (i) and (ii), which have been confirmed experimentally.

$$(CH_3)_3C-C(CH_3)_3 \quad + \quad \tfrac{1}{2}O_2 \quad = \quad 2i-C_4H_8 \quad + \quad H_2O \quad (s)$$

$$\Delta P \quad = \quad 1.5\Delta[TMB] \quad = \quad 0.75[i-C_4H_8] \quad (i)$$

$$-d[TMB]/dt \quad = \quad k_1[TMB]^1[O_2]^0 \quad (ii)$$
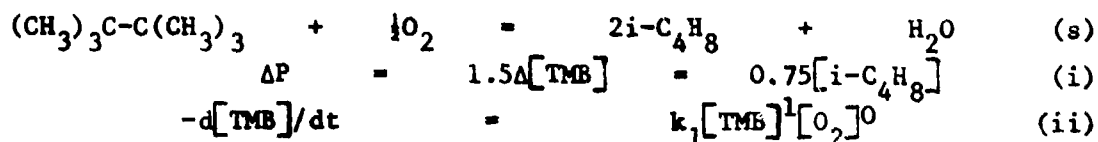
However, the experimental rate constant k_{obs}, based on expression (i), increases slightly (ca.10-20%) with TMB concentration over the range 0.25-4 Torr, and with addition of inert gas. This is attributed to a slight contribution from attack of OH and HO_2 radicals on TMB as the result

of the additional reactions (4)-(9) given below.

$$HO_2 \quad + \quad TMB \quad = \quad (CH_3)_3C-C(CH_3)_2CH_2 \quad + \quad H_2O_2 \quad (4)$$

$$HO_2 \quad + \quad HO_2 \quad = \quad H_2O_2 \quad + \quad O_2 \quad (5)$$

$$H_2O_2 \quad + \quad M \quad = \quad 2OH \quad + \quad M \quad (6)$$

$$H_2O_2 \quad \xrightarrow{\text{surface}} \quad H_2O \quad + \quad \tfrac{1}{2}O_2 \quad (7)$$

$$OH \quad + \quad TMB \quad = \quad (CH_3)_3C-C(CH_3)_2CH_2 \quad + \quad H_2O \quad (8)$$

$$(CH_3)_3C-C(CH_3)_2CH_2 \quad = \quad i-C_4H_8 \quad + \quad t-C_4H_9 \quad (9)$$

Studies[5] of the addition of TMB to the $H_2 + O_2$ reaction, discussed in
section (2) have shown that reaction (9) is the predominant reaction of the
TMB radical.

Use of a computer program, based on a stationary state treatment of
the radical concentrations and a Runge-Kutta integration of the differential
equations for the molecular species, has allowed the evaluation of the
rate constants k_1 and $k_4/k_5^{\frac{1}{2}}$ from studies over a range of TMB concentration
and total pressure. The chain contribution from reactions (4) and (8)
is only about 15% of the total reaction rate and is almost independent
of temperature between 420-540°C.

The corrected values of k_{obs} give a good s ight line plot of
log k_1 against 1/T over the range 420-540°C, with Arrhenius parameters
$A_1 = 1.2 \times 10^{17}$ s^{-1}, $E_1 = 295.4 \pm 1.5$ kJ mol^{-1}, which may be compared with
$A_1 = 2 \times 10^{16}$ s^{-1}, $E_1 = 286.5$ kJ mol^{-1} over the range 713-868°C,
obtained by Tsang[12] using a shock tube. Combination of Tsang's data,
suitably corrected, with the present data gives $A_1 = 6.0 \times 10^{16}$ s^{-1},
$E_1 = 290.4 \pm 1.5$ kJ mol^{-1} over the range 420-868°C. Combination of
the value of E_1 with that for the reverse reaction and with other thermodynamic
data gives the enthalpy of formation $\Delta_f H^o_{298} = 44.0 \pm 4.0$ kJ mol^{-1} for the
$t-C_4H_9$ radical, which is at least 10 kJ mol^{-1} higher than previously accepted
values. The value of $\Delta_f H^o_{298}$ leads to a bond dissociation energy D^o_{298}(t-Bu – H)
of 396.6 kJ mol^{-1}, which again is significantly higher than the previously
accepted value of 382 kJ mol^{-1}. Recommended values for the bond dissociation
energies in the C_1-C_4 alkanes are given later.

This work has been published.[13]

(b)   The reaction of HO_2 radicals with 2,2,3,3-tetramethylbutane

The increase in the observed value of the rate constant k_{obs}, obtained from expression (i), with increase in TMB concentration and on addition of inert gas is due to a small chain contribution (chain length less than unity) from reactions (4) and (8).   At the lowest temperatures (420 and 440°C) this is predominantly due to reaction (4), but as the temperature rises, the increased dissociation of H_2O_2 causes an increasing contribution from reaction (8);   at the same time the contribution from HO_2 attack decreases because reaction (5) becomes increasingly dominant as the concentration of radicals increases. Computer interpretation of the mechanism involving reactions (1)-(9) gives a preliminary value of $k_4 = 1.7 \times 10^4$ at 440°C.   However, although the individual values of the surface termination constant k_3 and the homogeneous termination constant k_5 are known, the total termination rate is not the sum of the two individual termination rates because of interaction between the homogeneous termination, which gives a uniform concentration of radicals across the reaction vessel, and the surface destruction, which gives a diffusion-controlled profile.   The occurrence of homogeneous termination increases the concentration gradient near the vessel surface, so that the rate of surface termination is greater than when homogeneous termination is absent.   There has been no previous study of the extent of this interaction.   Calculations with linear homogeneous termination, where the differential equations can be integrated, shows that the total termination rate may be increased by as much as 20%.   With mutual termination, the differential equationshave to be solved by numerical methods, and this work is in progress.

The value quoted for $k(HO_2 + TMB)$ represents the first direct determination of a rate constant for the HO_2 radical with an alkane.   This value was reported[11] at the Seventeenth International Combustion Symposium.

(c)   The molecular decomposition of 2,2,3,3-tetramethylbutane

A small amount (ca. 1%) of i-butane is found in the decomposition of TMB in the presence of O_2.   The rate of production of i-butane is first order in TB, and is independent of the concentration of O_2, of inert gas addition, and of vessel diameter.   These observations leave as the only
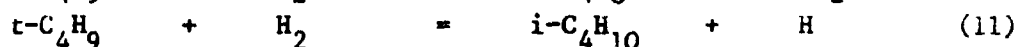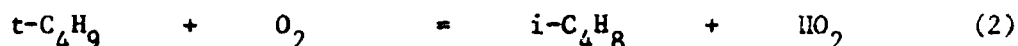
possibility a molecular mechanism for i-butane formation.

$$(CH_3)_3C-C(CH_3)_3 \quad = \quad i-C_4H_{10} \quad + \quad i-C_4H_8 \qquad (10)$$
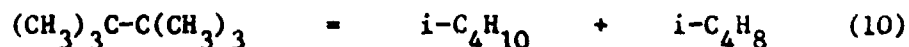
Study of the molecular decomposition between 420 -540°C gives the Arrhenius parameters A_{10} = 7.8 x 10^{13} s^{-1}, E_{10} = 275 $\pm$ 1.5 kJ mol^{-1}. The A factor is consistent with that expected for a four-centre transition state. These parameters appear to be the first reported for the non-chain, molecular decomposition of an alkane. This work has been published.[14]

(d) Reactions of t-butyl radicals

The basic mechanism involving reactions (1)-(3) indicates that the decomposition of TMB in the presence of O_2 offers a controlled source of t-butyl radicals. If H_2 is added, $i-C_4H_{10}$ is formed by reaction (11), and the competition between reactions (2) and (11) gives expression (iii).

$$t-C_4H_9 \quad + \quad O_2 \quad = \quad i-C_4H_8 \quad + \quad HO_2 \qquad (2)$$

$$t-C_4H_9 \quad + \quad H_2 \quad = \quad i-C_4H_{10} \quad + \quad H \qquad (11)$$

$$d[i-C_4H_{10}]/d[i-C_4H_8] \quad = \quad k_{11}[H_2]/k_2[O_2] \qquad (iii)$$

In using equation (iii), allowance must be made for the occurrence of reactions (9) and (10) in which i-butene is formed but not via the $t-C_4H_9$ radical, and for reaction (10) which forms i-butane by a molecular process. Because of the small yields of i-butane, high ratios (100-300) of $[H_2]/[O_2]$ must be used. The ratio $d[i-C_4H_{10}]/d[i-C_4H_8]$ is found to be proportional to $[H_2]/[O_2]$ as predicted by equation (iii), and the ratio k_2/k_{11} varies from 11,950 to 3,180 over the temperature range 440-540°C, corresponding to values of A_2/A_{11} = 0.35 $\pm$ 0.10, $(E_{11} - E_2)$ = 61.9 $\pm$ 2.0 kJ mol^{-1}. Use of the known value of k_{-11} and of thermochemical data for reaction (11) gives the values A_{11} = 2.30 x 10^9 dm^3 $mol^{-1}s^{-1}$, E_{11} = 71.0 $\pm$ 6.0 kJ mol^{-1}, A_2 = 8.0 x 10^8 dm^3 mol^{-1} s^{-1}, E_2 = 9.1 $\pm$ 10 kJ mol^{-1}. Although subject to some uncertainty, the low value for E_2 confirms the view that reactions of alkyl radicals with O_2 to give the conjugate alkene have a low activation energy.

The data are most self-consistent with a value of $\Delta_f H^O_{298}(t-C_4H_9)$ = 16.1 kJ mol^{-1}. This corresponds to a value of $D^O_{298}(t-C_4H_9 - H)$ of 392.7 kJ mol^{-1}, some 10 kJ mol^{-1} higher than currently accepted values. Suggested

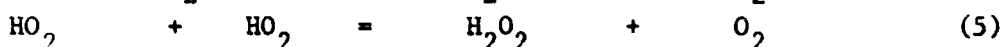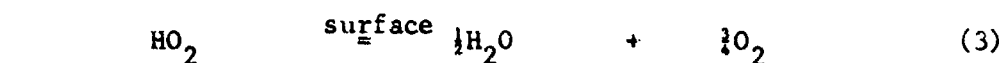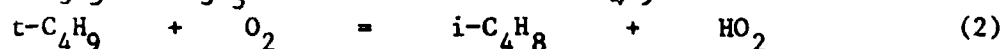values for C_2H_5 and $i-C_3H_7$ radicals, which are consistent with this value are given below.

Table 9
Enthalpies and C-H Bond Dissociation Energies for Alkyl Radicals

Radical	$\Delta_f H^o_{298}/(kJ \ mol^{-1})$	$D^o_{298}(R-H)/(kJ \ mol^{-1})$
CH_3	145.6 ± 1.0	438.4 ± 1.0
C_2H_5	118.0 ± 4.0	420.5 ± 4.0
$i-C_3H_7$	80.8 ± 4.0	402.5 ± 4.0
$t-C_4H_9$	37.6 ± 2.0	390.2 ± 2.0

The higher values listed in Table 9 have important kinetic conse_ences for the reactions of alkanes and alkyl radicals.

(e) Reactions of HO_2 radicals with alkanes and alkenes

There is considerable difficulty in finding a suitable source of HO_2 radicals in the temperature range 400-550°C, since with most methods of production of this radical, it is accompanied by more reactive radicals. However, the decomposition of TMB in the presence of O_2 offers a source of HO_2 radicals since, as already indicated, the mechanism is described with reasonable accuracy by reactions (1)-(3) and (5) below.

$$(CH_3)_3C-C(CH_3)_3 \quad = \quad 2t-C_4H_9 \qquad (1)$$
$$t-C_4H_9 \quad + \quad O_2 \quad = \quad i-C_4H_8 \quad + \quad HO_2 \qquad (2)$$

$$HO_2 \quad \xrightarrow{surface} \quad \tfrac{1}{2}H_2O \quad + \quad \tfrac{3}{4}O_2 \qquad (3)$$
$$HO_2 \quad + \quad HO_2 \quad = \quad H_2O_2 \quad + \quad O_2 \qquad (5)$$

An added alkane, such as ethane, will be removed by reaction (11), the predominant reaction of the C_2H_5 radicals produced being to form C_2H_4 by reaction (12).

$$HO_2 \quad + \quad C_2H_6 \quad = \quad C_2H_5 \quad + \quad H_2O_2 \qquad (11)$$
$$C_2H_5 \quad + \quad O_2 \quad = \quad HO_2 \quad + \quad C_2H_4 \qquad (12)$$
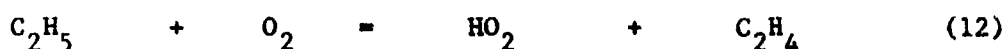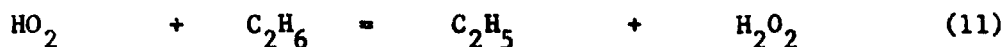
If HO_2 radicals are predominantly destroyed by reaction (3), the above scheme gives the rate expression (iv), whereas if reaction (5) predominates over (3), the rate expression (v) is obtained.

$$d[C_2H_4]/d[i-C_4H_8] \quad = \quad k_{11}[C_2H_6]/k_3 \qquad (iv)$$
$$d[C_2H_4]/d[i-C_4H_8] \quad = \quad 0.5k_{11}[C_2H_6]/(k_1k_5[TMB])^{\frac{1}{2}} \qquad (v)$$

Expression (iv) is found to be approximately correct at low temperatures and pressures, where the HO_2 concentration is low, whereas expression (v) is approached as the temperature and pressure increase. For accurate treatment, allowance must be made for the dissociation of hydrogen peroxide, reaction of HO_2 radicals with TMB, reaction of OH radicals both with ethane and TMB, reactions of C_2H_5 and $t-C_4H_9$ radicals with O_2 to give products other than the conjugate alkene, formation of i-butene by the molecular reaction (10) and by the decomposition reaction (9) of the TMB radical. All these effects are allowed for in a suitable computer treatment of the mechanism. Allowance is also made for a small amount of ethylene formed by a surface reaction, this process being most important at low TMB concentrations and low ethane concentrations. Preliminary interpretation gives a value of $k_{11} = 1.27 \times 10^4$ dm^3 $mol^{-1}s^{-1}$ at $440^\circ C$, but more precise values, particularly at higher temperatures must await an examination of the interaction between homogeneous and surface termination, discussed in section (4b).

The above studies with ethane have shown that the decomposition of TMB in the presence of O_2 provides a very convenient source of HO_2 radicals and a detailed study of their reactions with a wide range of alkanes and alkenes is planned. Very few rate constants for these reactions are available. Preliminary studies have been made with addition of i-butene. Since this is a primary product from the TMB + O_2 system, elucidation of its reactions is important in enabling the TMB + O_2 system to be used a long way into reaction, where products formed from i-butene will be important.

(f)   The oxidation of TMB in boric-acid-coated vessels

The decomposition of TMB in the presence of O_2, described in the preceding sections, has been carried out in KCl-coated vessels so that HO_2 radicals and H_2O_2 are efficiently destroyed, thus minimising the role of OH radicals formed by dissociation of H_2O_2. However, as the temperature, concentration of inert gas, and concentration of TMB increase, the concentration of HO_2 rises and reaction (5) competes increasingly with reaction (3).

$$HO_2 \xrightarrow{\text{surface}} \tfrac{1}{2}H_2O + \tfrac{3}{4}O_2 \qquad (3)$$

$$HO_2 + HO_2 = H_2O_2 + O_2 \qquad (5)$$
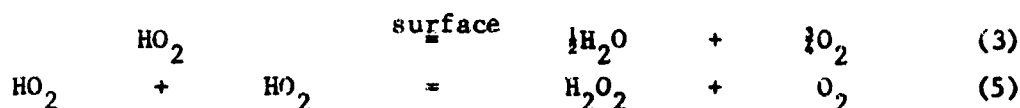
Under these conditions, calculation of the radical concentration is not easy because of the interaction between the diffusion-controlled profile of radical concentration across the vessel, and the uniform concentration resulting from homogeneous termination. This can be avoided by the use of aged boric-acid-coated vessels which, as previous studies of the $H_2 + O_2$ reaction have shown, are highly inefficient for the destruction of HO_2 and H_2O_2. Computer treatment of the mechanism has shown that as a consequence there is a significant decrease in the HO_2 concentration. The treatment shows that the reaction accelerates sharply with time due to the decomposition of H_2O_2 by reaction (6).

$$H_2O_2 \quad + \quad M \quad = \quad 2OH \quad + \quad M \qquad (6)$$
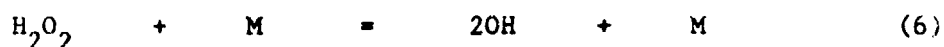
Preliminary studies have been made at $500^\circ C$ so that the ageing of the surface can be checked using the known characteristics of the $H_2 + O_2$ reaction at this temperature. The marked autocatalytic behaviour has been confirmed, but the reaction in consequence is rather fast for initial studies. The reaction is much slower at $440^\circ C$, 1% consumption of TMB occurring after about 300 seconds. At this point in the reaction, $i-C_4H_8$ is the sole product of any significance.

It is hoped that the increased concentration of OH radicals relative to HO_2 in this type of vessel may enable reactions of OH with the additive to be investigated.

5. The oxidation of 2,2,3-trimethylbutane

Although the steric hindrance around the central C-C link in 2,2,3-trimethylbutane (TRIMB) is less than in 2,2,3,3-tetramethylbutane (TMB), it is still sufficient for the decomposition to be reasonably fast in the temperature range $480-500^\circ C$. Since the $t-C_4H_9$ and $i-C_3H_7$ radicals predominantly react with O_2 to give the conjugate alkene and HO_2, the following simple scheme forms the basis of the mechanism in KCl-coated vessels where HO_2 radicals are efficiently destroyed at the surface.

$$(CH_3)_3C-CH(CH_3)_2 \quad = \quad t-C_4H_9 \quad + \quad i-C_3H_7 \qquad (13)$$

$$t-C_4H_9 \quad + \quad O_2 \quad = \quad i-C_4H_8 \quad + \quad HO_2 \qquad (2)$$

$$i-C_3H_7 \quad + \quad O_2 \quad = \quad C_3H_6 \quad + \quad HO_2 \qquad (14)$$

$$HO_2 \quad \xrightarrow{\text{surface}} \quad \tfrac{1}{2}H_2O \quad + \quad \tfrac{3}{4}O_2 \qquad (3)$$
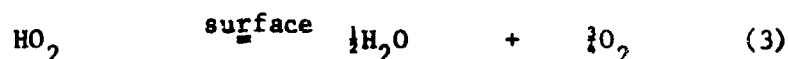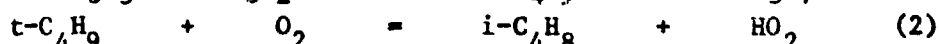
This simple mechanism gives the rate expression (vi), exactly analogous to expression (i) obtained with TMB.
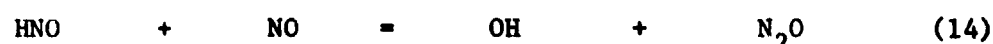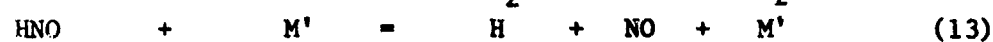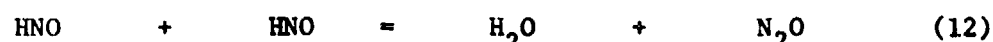
$$-d[TRIMB]/dt = k_{13}[TRIMB]^1[O_2]^0 \qquad (vi)$$

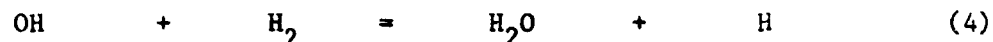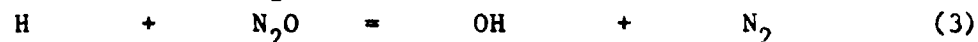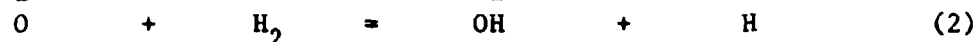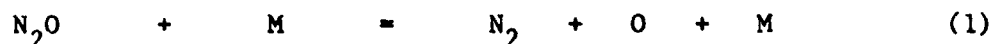Experimentally the rate is found to be zero order in O_2, but the observed rate constant k_{obs} increases with the concentration of TRIMB because of the significant chain contribution from HO_2 and OH attack on TRIMB, as in the case of TMB. By a double extrapolation of the observed rate constant k_{obs} to zero extent of reaction in a given initial concentration of TRIMB, and to zero initial concentration of TRIMB, accurate values of k_{13} may be obtained. These may be combined with the values obtained by Tsang to give $A_{13} = 2.9 \times 10^{16}$, $E_{13} = 305 \pm 2$ kJ mol^{-1}. The implications of this value for the thermochemistry of i-C_3H_7 and t-C_4H_9 radicals are being examined.

From the variation of k_{obs} with the concentration of TRIMB, a preliminary estimate of $k_{15} = (3.1 \pm 0.6) \times 10^5$ dm^3 mol^{-1}s^{-1} has been obtained.

$$HO_2 + (CH_3)_3C-CH(CH_3)_2 = (CH_3)_3C-C(CH_3)_2 + H_2O_2 \qquad (15)$$
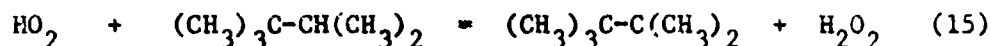
6. The reaction between hydrogen and nitrous oxide

The reaction between hydrogen and nitrous oxide has been studied mass spectrometrically at 500°C in a Pyrex vessel to confirm the mechanism below suggested by a study of the reaction at 600°C, and to obtain the activation energies of some of the reactions involved.

N_2O	+	M	=	N_2	+	O	+ M	(1)
O	+	H_2	=	OH	+	H		(2)
H	+	N_2O	=	OH	+	N_2		(3)
OH	+	H_2	=	H_2O	+	H		(4)
H	+	N_2O	=	NH	+	NO		(7)
NH	+	N_2O	=	HNO	+	N_2		(8)
H	+	HNO	=	H_2	+	NO		(9)
OH	+	HNO	=	H_2O	+	NO		(10)
H + NO	+	M'	=	HNO	+	M'		(11)
HNO	+	HNO	=	H_2O	+	N_2O		(12)
HNO	+	M'	=	H + NO	+	M'		(13)
HNO	+	NO	=	OH	+	N_2O		(14)
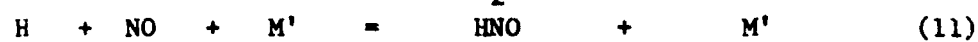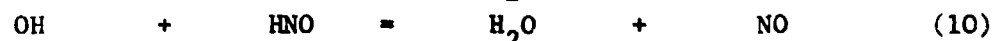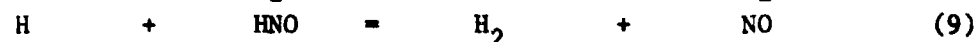
The behaviour of the reaction at $500^{\circ}C$ is very similar to that at $600^{\circ}C$. Nitric oxide is formed as a minor product, reaching a maximum concentration and then decreasing as the reaction proceeds. The self-inhibition characteristics of the reaction are due to the marked retarding effect of nitric oxide on the reaction. Attention has been concentrated on the $[NO]$, time profile for the mixture $[N_2O] = [H_2] = [Ar] = 100$ Torr and on the initial rates of nitrogen formation when small amounts of nitric oxide (0.1-5 Torr) are added to this mixture. This avoids the difficulties caused by uncertain coefficients for H_2 and Ar relative to N_2 as M in reaction (1) when the concentrations of the main reactants are varied.

Use of a computer treatment already developed to interpret the results at $600^{\circ}C$ shows that, as at $600^{\circ}C$, several combinations of rate constants will give a satisfactory interpretation of the results. Work is continuing to establish the best combination of rate constants and to use the computer program to examine what experiments might provide further information on this system.

Some studies have been made involving the addition of ethane to slowly reacting mixtures of $H_2 + N_2O$ at $550^{\circ}C$ with the intention of using the system as a source of H and OH radicals in the absence of O_2. The major product initially is ethylene, but it rapidly reaches a steady concentration, probably due mainly to the equilibrium (15).

$$H \quad + \quad C_2H_4 \quad = \quad C_2H_5 \quad\quad\quad (15)$$
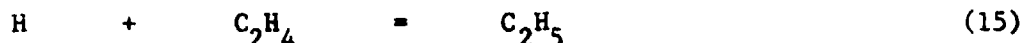
Once equilibrium has been established, methane becomes the major product and the kinetic features of the reaction suggest that it is produced by reactions (16) and (17).

$$H \quad + \quad C_2H_5 \quad = \quad 2CH_3 \quad\quad\quad (16)$$
$$CH_3 \quad + \quad H_2 \quad = \quad CH_4 \quad + \quad H \quad\quad\quad (17)$$
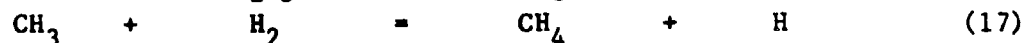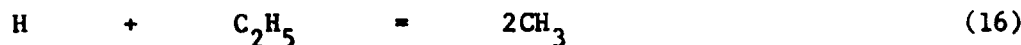
It was hoped that alkoxy radicals might be produced by reaction (18), so that their behaviour could be investigated, but no evidence for this reaction has been found.

$$C_2H_5 \quad + \quad N_2O \quad = \quad C_2H_5O \quad + \quad N_2 \quad\quad\quad (18)$$
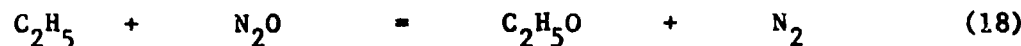
Rate constants obtained for reactions of $i-C_4H_9$, tetramethylbutyl, and 2,2,3-trimethylbutyl radicals are given in the Appendix.

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    mixtures of hydrogen and oxygen".
    R. R. Baldwin, R. W. Walker, and Robert W. Walker.
    J. Chem. Soc., Faraday I, in the press.

Publications / continued

11. "The reaction of t-butyl radicals with hydrogen and with oxygen".
    G. A. Evans and R. W. Walker.
    J. Chem. Soc., Faraday I, in the press.

12. "Decomposition of 2,2,3-trimethylbutane in the presence of oxygen".
    R. R. Baldwin, R. W. Walker, and Robert W. Walker.
    J. Chem. Soc., Faraday I, submitted for publication.

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Conferences attended and Lectures presented

Dr. Walker attended the "Fifth International Symposium on Gas Kinetics", held in Manchester in July 1977 and presented a paper entitled "The Decomposition of Tetramethylbutane in the Presence of Oxygen".

Professor Baldwin gave an invited lecture entitled "Problems and Progress in Hydrocarbon Oxidation", at the Autumn meeting of the Chemical Society, held at the University of Aberdeen in September 1977.

Professor Baldwin and Dr. Walker attended the Seventeenth (International) Combustion Symposium held at the University of Leeds in August 1978, and presented a paper entitled "Rate Constants for Reactions of HO_2 Radicals with Alkanes, Aldehydes, and Related Compounds".

Dr. Walker attended the U.S. Air Force Contractors' Meeting held at Dayton, Ohio, in October 1978, and presented a paper entitled "Rate Constants for H, OH, and HO_2 Radical Attack on Alkanes".

Professor Baldwin, Dr. Walker, and their research group attended a one-day research meeting on "Combustion" at the University of York in May 1979.

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Personnel

Mrs. J. P. Bennett, who was financed under Grant AFCSR 73-2450, has successfully submitted for the Ph.D. degree.

Mr. R. W. Walker, financed by a Science Research Council Award, who joined the group in September 1975, has completed his period of study and

will be submitting his Ph.D. thesis shortly. He has now taken up a position with Imperial Chemical Industries Ltd.

Mr. G. A. Evans, who joined the research group in 1975, and was financed under Grants AFOSR 73-2450 and AFOSR 77-3215, has completed his period of study and will shortly be submitting his Ph.D. thesis. He has now obtained a teaching post at Knaresborough Grammar School.

Mr. A. P. Keen (B.Sc., Hull 1977) joined the group in September 1977, financed by Grant AFOSR 77-3215.

Mr. I. A. Pickering (B.Sc., Hull 1978) joined the research group as technician in July 1978 and is financed by the University.

Mr. D. G. Malcolm (B.Sc., Hull 1978) and Mr. M.W.M. Hisham (B.Sc., University of Sri Lanka) joined the research group in September 1978 and were financed by Grant AFOSR 77-3215. Mr. Malcolm will take up the post of Research Assistant, financed by the Science Research Council, as from October 1979.

Miss A. Sutcliffe (B.Sc., Hull 1979) will join the group in September 1979 and will be financed under Grant AFOSR 77-3215.

The Science Research Council have made a grant of £33,050 to Professor Baldwin and Dr. Walker for the purchase of Perkin Elmer gas chromatographic equipment, and to provide for a Research Assistant.

Informal discussions have taken place with Dr. Barnard of University College, London, Dr. Simmons of the University of Manchester Institute of Science and Technology, Professor Gray, Professor Williams, Professor Dixon-Lewis and Dr. Griffiths of Leeds University, Dr. Golden of the Stanford Research Institute, Professor Waddington of York University, Dr. Turner of Bradford University, Dr. D. Booth of Newcastle Polytechnic, Dr. Dryer of Princeton University, and Dr. K. Booth of Imperial Chemical Industries Ltd.

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Appendix

Table 1

Rate Constants for the $i-C_4H_9$ Radical System at $480°C$

Reaction		$k/dm^3,mol,s$	note
$CH_3CH(CH_3)CH_2$	$= C_3H_6 + CH_3$	8.8×10^4	
$CH_3CH(CH_3)CH_2 + O_2$	$= i-C_4H_8 + HO_2$	6.8×10^7	
$CH_3CH(CH_3)CH_2 + O_2$	$= CH_3CH(CH_3)CH_2O_2$	1.0×10^9	a
$CH_3CH(CH_3)CH_2O_2$	$= CH_3CH(CH_3)CH_2 + O_2$	2.6×10^6	b
$CH_3CH(CH_3)CH_2O_2$	$= CH_3CH(CH_2OOH)CH_2$	4.45×10^4	b
$CH_3CH(CH_2OOH)CH_2$	$= CH_3CH(CH_3)CH_2O_2$	1.35×10^6	b
$CH_3CH(CH_3)CH_2O_2$	$= CH_3C(CH_3)(CH_2OOH)$	1.83×10^5	b
$CH_3C(CH_3)(CH_2OOH)$	$= CH_3CH(CH_3)CH_2O_2$	8.3×10^5	b
$CH_3CH(CH_2OOH)CH_2$	$= 3-methyloxetan + OH$	$(1-2) \times 10^6$	c
$CH_3C(CH_3)(CH_2OOH)$	$= isobutene \ oxide + OH$	1.8×10^6	c
$CH_3CH(CH_2OOH)CH_2 + O_2$	$= CH_3Ch(CH_2OOH)CH_2O_2$	1.0×10^9	a
$CH_3CH(CH_2OOH)CH_2O_2$	$= CH_3CH(CH_2OOH)CH_2 + O_2$	2.6×10^6	b
$CH_3C(CH_3)(CH_2OOH) + O_2$	$= CH_3C(CH_3)(CH_2OOH)O_2$	1.0×10^9	a
$CH_3C(CH_3)(CH_2OOH)O_2$	$= CH_3C(CH_3)(CH_2OOH) + O_2$	7.5×10^6	b
$CH_3CH(CH_2OOH)CH_2O_2$	$= CH_3CHO + 2HCHO + OH$	$(1-2) \times 10^6$	c
$CH_3C(CH_3)(CH_2OOH)O_2$	$= CH_3COCH_3 + HCHO + HO_2$	3.0×10^6	c
$CH_3C(CH_3)(CH_2OOH)$	$= CH_2=C(CH_3)CH_2OH + OH$	1.3×10^5	c
$CH_3C(CH_3)(CH_2OOH)$	$= CH_2=C(CH_3)CHO + OH + H_2$	1.3×10^5	c
$CH_3C(CH_3)(CH_2OOH)$	$= (CH_3)_2CHCHO + OH$	4.2×10^5	c

a Assumed value.

b The values are dependent on the calculated value of $K(R + O_2)$.

c The values are determined from maximum and minimum limits.

Table 2

Rate Constants for the Decomposition of tetramethylbutyl and 2,2,3-trimethylbutyl Radicals at $480°C$

Reaction		k/s^{-1}
$(CH_3)_3CC(CH_3)_2$	$= (CH_3)_2C=C(CH_3)_2 + CH_3$	1.4×10^3
$(CH_3)_3CC(CH_3)_2CH_2$	$= t-C_4H_9 + i-C_4H_8$	1.9×10^6
$(CH_3)_3CC(CH_3)_2CH_2$	$= (CH_3)_3CC(CH_3)=CH_2 + CH_3$	1.1×10^4